LINEAR RESPONSE THEORY OR DENSITY FUNCTIONAL PERTURBATION THEORY

MANY PHYSICAL PROPERTIES CAN BE EXPRESSED AS DERIVATIVES OF THE TOTAL ENERGY

E.G.: E = ENERGIA PER CELLA ELEMENTARE

FIRST ORDER DERIVATIVES

- FORCES ON IONS $\vec{F}_I = -\frac{dE}{dR_I}$
- ELECTRIC POLARISATION $\vec{M} = -\frac{dE}{d\vec{E}_{ELEC.}}\Omega$ (Ω = VOLUME CELLA ELEM.)
- PRESSURE $P = -\frac{dE}{dV}$
- DENSITY $\rho(\vec{r}) = \frac{dE}{dV_{EXT}(\vec{r})}$

SECOND ORDER DERIVATIVES

- DYNAMICAL MATRIX FOR PHONON-CALCULATIO

$$\overleftrightarrow{D}_{IJ} = \frac{d\vec{F}_I}{dR_J} = -\frac{d^2E}{d\vec{R}_J dR_I}$$

- ELECTRIC SUSCEPTIBILITY

$$\overleftrightarrow{\chi} = -\frac{d\vec{M}}{d\vec{E}_{ELEC.}}\Omega = -\frac{d^2E}{d\vec{E}_{ELEC}\,d\vec{E}_{ELEC}}\Omega$$

SECOND ORDER DERIVATIVES

- EFFETIVE CHARGES FOR INFRARED ACTIVITY

$$\overleftrightarrow{Z}^*_I = \Omega \frac{d\vec{M}}{d\vec{R}_I} = -\frac{d^2E}{d\vec{R}_I d\vec{E}_{ELEC}} = -\frac{d^2E}{d\vec{E}_{ELEC} d\vec{R}_I} = \frac{d\vec{F}_I}{d\vec{E}_{ELEC}}$$

- DENSITY-DENSITY RESPONSE OR SUSCEPTIBILITY (IMPORTANT FOR MICROSCOPIC SCREENING)

$$\chi(\vec{r}, \vec{r}') = \frac{d\rho(\vec{r})}{dV_{EXT}(\vec{r}')} = \frac{d^2E}{dV_{EXT}(\vec{r}') dV_{EXT}(\vec{r})}$$

THIRD ORDER DERIVATIVES

- NON LINEAR ELECTRIC SUSCEPTIBILITY (FOR 3rd ORDER HARMONIC GENERATION)

$$\Omega \chi^{(2)}_{\alpha\beta\gamma} = -\frac{dE}{dE^{\alpha}_{ELEC} dE^{\beta}_{ELEC} dE^{\gamma}_{ELEC}}$$

- RAMAN ACTIVITY

$$\vec{A}_{\alpha\beta} = \frac{d\chi_{\alpha\beta}}{d\vec{R}_I} = -\frac{dE}{d\vec{R}_I dE^{\alpha}_{ELEC} dE^{\beta}_{ELEC}}$$

- ANHARMONIC FORCE CONSTANCES (PHONON LIFE-TIME, THERMAL EXPANSION, THERMAL CONDUCTIVITY)

$$\overleftrightarrow{C}_{I,J,K} = -\frac{dE}{d\vec{R}_I d\vec{R}_J d\vec{R}_K}$$

DERIVATIVES BY PERTURBATION THEORY

WHY?

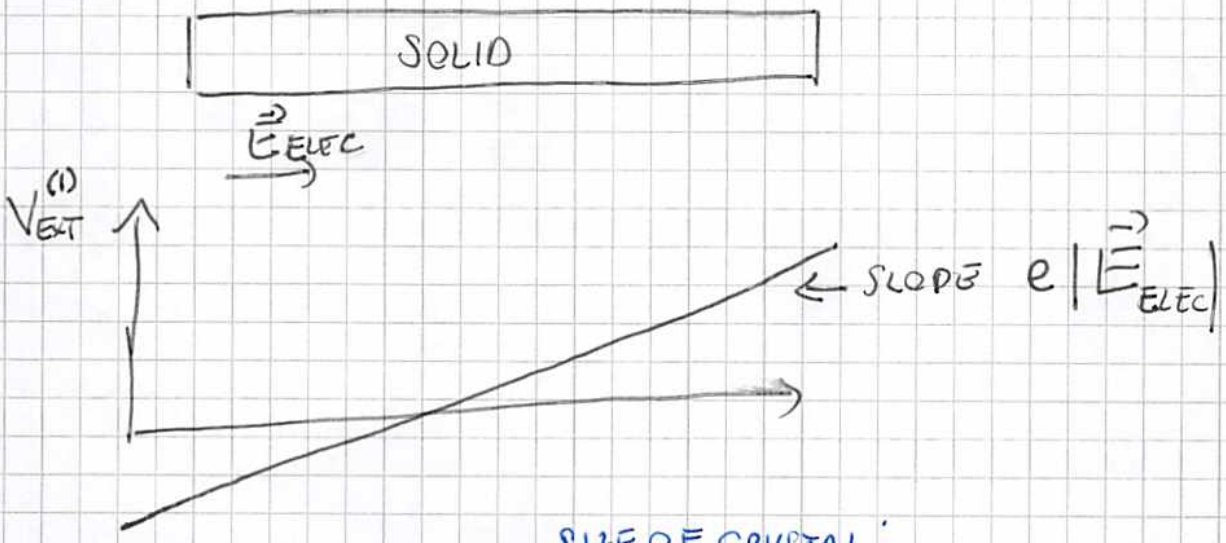
(A) • PERTURBATION THEORY ASSOCIATES THE PROPERTY TO THE BAND STRUCTURE

⇓

PHYSICAL INTERPRETATION

(B) • IN SOLIDS SOME PROPERTIES ONLY DEFINED FOR INFINITESIMAL PERTURBATIONS

E.G. THOSE ASSOCIATED TO AN UNIFORM ELECTRIC FIELD



IF $|\vec{E}_{ELEC}| e \cdot L >$ BAND GAP ← SIZE OF CRYSTAL

ELECTRONS ACCUMULATE ON ONE SIDE OF THE SOLID

IN REALITY THE SOLID REMAINS IN A METASTABLE STATE ($\neq$GS) IF THE FIELD IS NOT TOO STRONG

IF $|E_{ELEC}| < E_{ELEC\ BREAKDOWN}$

$$E_{ELEC\ BREAKDOWN} \sim \frac{E_{GAP}}{e m L_{CELL}}$$

$L_{CELL} \sim$ SIZE UNIT CELL

m = SMALL NUMBER

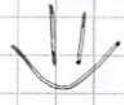
PERTURBATION THEORY : RESPONSE OF THE METASTABLE STATE

- IF WE USE PERTURBATION THEORY NON-PERIODIC BUT MONOCROMATIC PERTURBATIONS

$$V^{(1)}_{\vec{q}}(\vec{r}) = e^{i\vec{q}\cdot\vec{r}}\, U_{\vec{q}}(\vec{r}) \qquad U_{\vec{q}}(\vec{r}) = \text{PERIODIC WITH LATTICE}$$

E.G. PERTURBATION ASSOCIATED TO A PHONON WITH MOMENTUM $\vec{q}$

CAN BE EXPRESSED AS MATRIX-ELEMENTS COMPUTED IN THE UNIT CELL



BIG ADVANTAGE FOR INTERPRETATION AND FOR COMPUTATION

DFT ANALYTIC DERIVATIVES

λ = PERTURBATION PARAMETER

THE PERTURBATION JUST ENTER IN THE ONE BODY PART OF THE HAMILTONIAN

THUS IN $V_{EXT}(\vec{r})$ (NOT FOR MAGNETIC FIELD AND ORBITAL MOTION BUT ALSO IN THIS CASE ONE BODY HAMILTONIAN)

$\Downarrow\Downarrow$

ONLY λ DEPENDENCE IN $V_{EXT}^{\lambda}(\vec{r})$

$$E^{DFT}(\lambda) = \min_{\{\psi_i\}} E[\{\psi_i\}, \lambda] = E[\{\psi_i^{\lambda}\}, \lambda]$$

$\{\psi_i\}$: SINGLE PARTICLES ORBITALS

$\{\psi_i^{\lambda}\}$: ORBITAL AT THE MINIMUM

FIRST DERIVATIVES (HELLMANN-FEYNMAN FOR DFT)

$$\frac{dE^{DFT}(\lambda)}{d\lambda} = \underbrace{\frac{\partial}{\partial \{\psi_i\}} E[\{\psi_i^{\lambda}\}, \lambda] \frac{d\{\psi_i^{\lambda}\}}{d\lambda}}_{=0 \text{ SINCE } \{\psi_i^{\lambda}\} \text{ MINIMIZE THE FUNCTIONAL}} + \frac{\partial}{\partial \lambda} E[\{\psi_i^{\lambda}\}, \lambda]$$

$$\boxed{\frac{dE^{DFT}(\lambda)}{d\lambda} = 2 \sum_{i=1}^{N/2} \langle \psi_i^{\lambda} | \frac{dV_{EXT}^{\lambda}}{d\lambda} | \psi_i^{\lambda} \rangle}$$

FOR FIRST DERIVATIVES WE JUST NEED THE UNPERTURBED KS EIGENSTATES

$|\psi_i^{(0)}\rangle \overset{\text{def}}{\equiv} |\psi_i^{\lambda}\rangle$ ROTATED SUCH THAT

$$H_{KS}\,|\psi_i^{(0)}\rangle = \varepsilon_i^{(0)}\,|\psi_i^{(0)}\rangle$$

P = PROJECTION IN THE OCCUPIED SPACE

$$P = \sum_{i=2}^{N/2} |\psi_i^{\lambda}\rangle\langle\psi_i^{\lambda}| = \sum_{i=1}^{N/2} |\psi_i^{(0)}\rangle\langle\psi_i^{(0)}|$$

$$\frac{dE^{DFT}}{d\lambda} = 2\,\mathrm{tr}\left[\, P\,\frac{dV_{\lambda}}{d\lambda}\,\right]$$

SECOND-ORDER DERIVATIVES (TWO PARAMETERS)

$$V_{EXT}^{\lambda,\eta}(\vec{r})$$

$$\frac{d^2 E^{DFT}(\lambda,\eta)}{d\eta\, d\lambda} = \frac{d}{d\eta}\left[2 \sum_{i=1}^{N/2} \langle \psi_i^{\lambda\eta} \left| \frac{dV_{EXT}^{\lambda,\eta}}{d\lambda} \right| \psi_i^{\lambda\eta} \rangle \right]$$

$$= 2 \sum_{i=1}^{N/2} \langle \psi_i^{\lambda\eta} \left| \frac{d^2 V_{EXT}^{\lambda,\eta}}{d\lambda\, d\eta} \right| \psi_i^{\lambda\eta} \rangle$$

$$+ 2 \sum_{i=1}^{N/2} \frac{d\langle \psi_i^{\lambda\eta}|}{d\eta} \left| \frac{dV_{EXT}^{\lambda,\eta}}{d\lambda} \right| \psi_i^{\lambda\eta} \rangle$$

$$+ 2 \sum_{i=1}^{N/2} \langle \psi_i^{\lambda\eta} | \, dV_{EXT} \frac{d|\psi_i^{\lambda,\eta}\rangle}{d\eta}$$

NOTATIONS $|\psi_i^{(1,0)}\rangle = \frac{d|\psi_i^{\lambda\eta}\rangle}{d\lambda}$

$|\psi_i^{(0,1)}\rangle = \frac{d|\psi_i^{\lambda\eta}\rangle}{d\eta}$

$$\frac{dV_{EXT}^{\lambda\eta}}{d\lambda} = V_{EXT}^{(1,0)}$$

$$\frac{dV_{EXT}^{\lambda\eta}}{d\eta} = V_{EXT}^{(0,1)}$$

...

...

WHERE

$$H_{KS} |\psi_i^{\lambda\eta}\rangle = \varepsilon_i^{\lambda\eta} |\psi_i^{\lambda\eta}\rangle$$

$$E^{DFT(1,1)} = 2\sum_{i=1}^{N/2}\left\{\langle\psi_i^{(0)}|V_{EXT}^{(1,1)}|\psi_i^{(0)}\rangle + \langle\psi_i^{(0,2)}|V_{EXT}^{(1,0)}|\psi_i^{(0)}\rangle + \langle\psi_i^{(0)}|V_{EXT}^{(1,0)}|\psi_i^{(0,1)}\rangle\right\}$$

ALTERNATIVE FORMULATION IN TERM OF THE DENSITY

$$E^{DFT(1,0)} = \int d^3r\, V_{EXT}^{(1,0)}(\vec{r})\,\rho^{(0)}(\vec{r})$$

$$E^{DFT(1,1)} = \int d^3r\, V_{EXT}^{(1,1)}(\vec{r})\,\rho^{(0)}(\vec{r}) + \int d^3r\, V_{EXT}^{(1,0)}(\vec{r})\,\rho^{(0,1)}(\vec{r})$$

$$\rho^{(0,1)}(\vec{r}) = 2\sum_{i=1}^{N/2}\left[\langle\psi_i^{(0,1)}|\vec{r}\rangle\langle\vec{r}|\psi_i^{(0)}\rangle + \langle\psi_i^{(0)}|\vec{r}\rangle\langle\vec{r}|\psi_i^{(0,1)}\rangle\right]$$

WHAT IS $|\psi_i^{(\nu)}\rangle$?

$$H_{KS}^{n}|\psi_i^{n}\rangle = \varepsilon_i^{n}|\psi_i^{n}\rangle \qquad \langle\psi_i^{n}|\psi_i^{n}\rangle = 1$$

$$H_{KS}^{n} = \frac{p^2}{2m_e} + V_H^{n}(\vec{r}) + V_{XC}^{n}(\vec{r}) + V_{EXT}^{n}(\vec{r})$$

$$H_{KS}^{(0)} = H_{KK}^{n}$$

$$H_{KS}^{(\nu)} = \frac{d H_{KS}^{n}}{d n} = V_{EXT}^{(1)}(\vec{r}) + V_H^{(1)}(\vec{r}) + V_{XC}^{(1)}(\vec{r})$$

$$V_H^{(1)}(\vec{r}) = \int d^3r' \frac{dV_H(\vec{r})}{d\rho(\vec{r}')}\rho^{(1)}(\vec{r}') = \int d^3r' \frac{d^2E_H}{d\rho(\vec{r})\,d\rho(\vec{r}')}\rho^{(1)}(\vec{r}')$$

$$= \int d^3r' \, K_H(\vec{r},\vec{r}')\rho^{(1)}(\vec{r}') = \int d^3r' \frac{e^2}{|\vec{r}-\vec{r}'|}\rho^{(1)}(\vec{r}')$$

KERNEL OF H ENERGY $= K_H(\vec{r},\vec{r}') = \dfrac{d^2E_H}{d\rho(\vec{r})\,d\rho(\vec{r}')} = \dfrac{e^2}{|\vec{r}-\vec{r}'|}$

$$V_{XC}^{(1)}(\vec{r}) = \int d^3r' \, K_{XC}(\vec{r},\vec{r}')\rho^{(1)}(\vec{r}')$$

KERNEL OF XC ENERGY $= K_{XC}(\vec{r},\vec{r}') = \dfrac{d^2E_{XC}}{d\rho(\vec{r})\,d\rho(\vec{r}')}$

IN LDA $K_{xc}^{LDA}(\vec{r},\vec{r}') = \delta(\vec{r}-\vec{r}')\, f_{xc}(\rho(\vec{r}))$

$$f_{xc}(\rho) = 2\frac{d\,\varepsilon_{xc}(\rho)}{d\rho} + \frac{d^2\varepsilon_{xc}(\rho)}{d\rho^2}\,\rho$$

BY PERTURBATION THEORY

$$|\psi_i^{(1)}\rangle = -\sum_{j\neq i}\frac{|\psi_j^{(0)}\rangle\langle\psi_j^{(0)}|H_{KS}^{(1)}|\psi_i^{(0)}\rangle}{\varepsilon_j^{(0)}-\varepsilon_i^{(0)}} + ia|\psi_i^{(0)}\rangle$$

$a\in\mathbb{R}$ $\left(\langle\psi_i^n|\psi_i^n\rangle = 1 \Rightarrow \frac{d(\langle\psi_i^n|\psi_i^n\rangle)}{dn} = 0 \Rightarrow\right.$

$\Rightarrow \langle\psi_i^{(1)}|\psi_i^{(0)}\rangle + \langle\psi_i^{(0)}|\psi_i^{(1)}\rangle = 0$

$\left.\Rightarrow -ia^* + ia = 0 \Rightarrow a\in\mathbb{R}\right)$

VALID IF $\varepsilon_i^{(0)} \neq \varepsilon_j^{(0)}$ FOR $i\neq j$ (PROBLEM WITH DEGENERATE STATES)

$P = \sum_{i=1}^{N/2} |\psi_i^{(0)}\rangle\langle\psi_i^{(0)}|$ PROJECTOR OVER OCCUPIED SUBSPACE

$Q = \mathbb{1} - P$ PROJ. OVER EMPTY SUBSPACE

$Q + P = \mathbb{1}$

IRRELEVANT IN EXPECTATION VALUES OF HERMITIAN OPERATOR

$|\psi_i^{(1)}\rangle = Q|\psi_i^{(1)}\rangle + P|\psi_i^{(1)}\rangle$

O = HERMITIAN OPERATOR (LIKE $|\vec{r}\rangle\langle\vec{r}|$ OR $V_{EXT}^{(1)}(\vec{r})$)

$$O^{(1)} = 2\sum_{i=1}^{N/2}\left[\langle\psi_i^{(1)}|O|\psi_i^{(0)}\rangle + \langle\psi_i^{(0)}|O|\psi_i^{(1)}\rangle\right]$$

$$= 2\sum_{i=1}^{N/2}\left[\langle\psi_i^{(1)}|QO|\psi^{(0)}\rangle + \langle\psi^{(0)}|OQ|\psi_i^{(1)}\rangle\right]$$

SINCE

$$\sum_{i=1}^{N/2}\left[\langle\psi_i^{(1)}|PO|\psi_i^{(0)}\rangle + \langle\psi_i^{(0)}|OP|\psi_i^{(1)}\rangle\right] =$$

$$= \sum_{\substack{i,j=1\\(\neq)}}^{N/2} -\left[\frac{\langle\psi_i^{(0)}|H^{(1)}|\psi_j^{(0)}\rangle\langle\psi_j^{(0)}|O|\psi_i^{(0)}\rangle}{\varepsilon_j^{(0)} - \varepsilon_i^{(0)}} + \frac{\langle\psi_i^{(0)}|O|\psi_j^{(0)}\rangle\langle\psi_j^{(0)}|H^{(1)}|\psi_i^{(0)}\rangle}{\varepsilon_j^{(0)} - \varepsilon_i^{(0)}}\right]$$

$= O$!

BY INTERCHANGE $i \leftrightarrow j$ DUMMY INDEXES THE SECOND TERM IS EQUAL TO − FIRST TERM

$$Q|\psi_i^{(1)}\rangle = -\sum_{j\in \text{EMPTY STATES}} \frac{|\psi_j^{(0)}\rangle\langle\psi_j^{(0)}|H_{KS}^{(1)}|\psi_i^{(0)}\rangle}{\varepsilon_j^{(0)} - \varepsilon_i^{(0)}}$$

$$G(\varepsilon) = \frac{1}{\varepsilon - H_{KS}^{(0)}}\,Q$$

GREEN FUNCTION PROJECTED IN EMPTY SPACE

$$Q|\psi_i^{(1)}\rangle = G(\varepsilon_i^{(0)})\,H_{KS}^{(1)}|\psi_i^{(0)}\rangle$$

TO RESUME WE HAVE TO SOLVE:

$$\begin{cases} H_{KS}^{(1)} = V_{EXT}^{(1)} + V_{Hxc}^{(1)} \\ V_{Hxc}^{(1)}(\vec{r}) = \int d^3r' \, K_{Hxc}(\vec{r},\vec{r}') \, \rho^{(1)}(\vec{r}') \\ \rho^{(1)}(\vec{r}) = \sum_{i=1}^{N/2} 2 \left[\langle \psi_i^{(1)} | Q | \vec{r} \rangle \langle \vec{r} | \psi_i^{(0)} \rangle + \langle \psi_i^{(0)} | \vec{r} \rangle \langle \vec{r} | Q | \psi_i^{(1)} \rangle \right] \\ Q|\psi_i^{(1)}\rangle = \dfrac{1}{\varepsilon_i^{(0)} - H_{KS}^{(0)}} Q \, H_{KS}^{(1)} |\psi_i^{(0)}\rangle \end{cases}$$

DENSITY-DENSITY RESPONSE

$$\chi(\vec{r},\vec{r}') = \frac{dE^{DFT}}{dV_{EXT}(\vec{r})\,dV_{EXT}(\vec{r}')} = \frac{d\rho(\vec{r}')}{dV_{EXT}(\vec{r})}$$

$$\Downarrow\Downarrow$$

FOR ANY PERTURBATION $V^{(1)}_{EXT}(\vec{r})$ KNOWING $\chi(\vec{r},\vec{r}')$ WE CAN OBTAIN THE INDUCED DENSITY $\rho^{(1)}(\vec{r})$

$$\rho^{(1)}(\vec{r}) = \int d^3r\, \chi(\vec{r},\vec{r}')\, V^{(1)}_{EXT}(\vec{r}')$$

IN MATRIX VECTOR NOTATION

$$\vec{\rho}^{(1)} = \overleftrightarrow{\chi}\, \vec{V}^{(1)}_{EXT}$$

WHERE THE VECTOR / MATRIX COMPONENT ARE LABELED BY $\vec{r}$ AND $\vec{r}'$

KNOWING $\chi(\vec{r},\vec{r})$ WE CAN ALSO OBTAIN THE SCREENED POTENTIAL FELT BY THE ELECTRONS

$$V^{(1)}_{KS}(\vec{r}) = \int d^3r'\, K_{Hxc}(\vec{r},\vec{r}')\rho^{(1)}(\vec{r}') + V^{(1)}_{EXT}(\vec{r})$$

$$\rho^{(1)}(\vec{r}') = \int d^3r''\, \chi(\vec{r}',\vec{r}'')\, V^{(1)}_{EXT}(\vec{r}'')$$

IN MATMX VECTOR NOTATION

$$\vec{V}^{(1)}_{KS} = \left(\overleftrightarrow{K}_{Hxc}\,\overleftrightarrow{\chi} + \overleftrightarrow{1}\right) V^{(1)}_{Ext}$$

BY ANALOGY WITH ELECTROSTATICS

$$\vec{V}^{(1)}_{KS} = \overleftrightarrow{\varepsilon}^{-1} V^{(1)}_{EXT}$$

$$\overleftrightarrow{\varepsilon}^{-1} = \left(\overleftrightarrow{1} + \overrightarrow{K}_{HxC}\overleftrightarrow{\chi}\right) \quad (*)$$

COMPUTATION OF $\chi(\vec{r},\vec{r}')$

WE DEFINE THE BARE (NON-INTERACTING) RESPONSE AS $\chi^b(\vec{r},\vec{r}')$ FROM

$$\rho^{(1)}(\vec{r}) = \int d^3r'\, \chi^b(\vec{r},\vec{r}')\, V^{(1)}_{KS}(\vec{r}')$$

FROM PERTURBATION THEORY (NOTE THAT: $\frac{dV_{KS}(\vec{r})}{dV_{KS}(\vec{r}')} = \delta(\vec{r}-\vec{r}') = |\vec{r}\rangle\langle\vec{r}'|$)

$$\chi^b(\vec{r},\vec{r}') = 4\sum_{i=1}^{N/2}\left[\langle\psi_i^{(0)}|\vec{r}\rangle\langle\vec{r}|Q\,\frac{1}{\varepsilon_i^0 - H^{(0)}}Q|\vec{r}'\rangle\langle\vec{r}'|\psi_i^0\rangle\right]$$

IN VECTOR NOTATION

$$\vec{\rho}^{(1)} = \overleftrightarrow{\chi}^b \vec{V}^{(1)}_{KS} = \overleftrightarrow{\chi}^b\left(1\!\!1 + \overrightarrow{K}_{HxC}\overleftrightarrow{\chi}\right)\vec{V}_{EXT}$$

$$\vec{\rho}^{(1)} = \overleftrightarrow{\chi}\,\vec{V}_{EXT}$$

$$\overleftrightarrow{\chi} = \overleftrightarrow{\chi}^b\left(1\!\!1 + \overrightarrow{K}_{HxC}\overleftrightarrow{\chi}\right) \quad (*,*)$$

$$\left(1\!\!1 - \overleftrightarrow{\chi}^b\overrightarrow{K}_{HxC}\right)\overleftrightarrow{\chi} = \overleftrightarrow{\chi}^b$$

$$\overleftrightarrow{\chi} = \frac{1}{1 - \overleftrightarrow{\chi}^b \overleftrightarrow{K}_{HXC}} \overleftrightarrow{\chi}^b$$

$\overleftrightarrow{\chi}$: INTERACTING RESPONSE

$\overleftrightarrow{\chi}^b$: NON INTERACTING DENSITY - DENSITY RESPONSE

(**)

$$\overleftrightarrow{K}_{HXC}\overleftrightarrow{\chi} = \overleftrightarrow{K}_{HXC}\overleftrightarrow{\chi}^b\left(\overleftrightarrow{\varepsilon}^{-1}\right)$$

BY (A)

$$\overleftrightarrow{\varepsilon}^{-1} - 1\!\!1 = \overleftrightarrow{K}_{HXC}\overleftrightarrow{\chi}^b\left(\overleftrightarrow{\varepsilon}^{-1}\right)$$

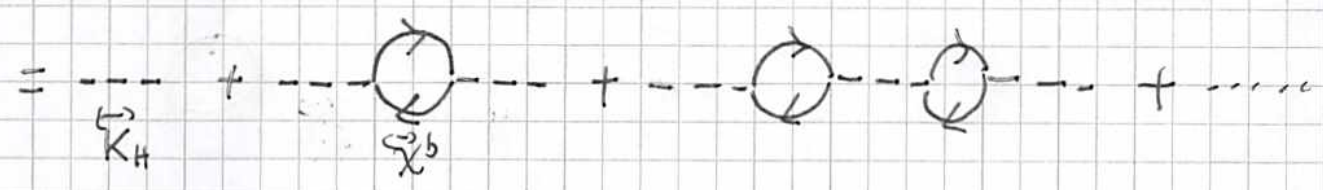
$$\overleftrightarrow{\varepsilon}^{-1} = \frac{1}{1\!\!1 - \overleftrightarrow{K}_{HXC}\overleftrightarrow{\chi}^b}$$

IN RPA APPROXIMATION $\overleftrightarrow{K}_{XC}$ IS NEGLECTED

$$\overleftrightarrow{\varepsilon}^{-1\,RPA} = \frac{1}{1\!\!1 - \overleftrightarrow{K}_H\overleftrightarrow{\chi}^b}$$

(STATICALLY) SCREENED e-e INTERACTION IN RPA

$$W = \overleftrightarrow{\varepsilon}^{-1\,RPA}\overleftrightarrow{K}_H = \frac{1}{1\!\!1 - \overleftrightarrow{K}_H\overleftrightarrow{\chi}^b}\overleftrightarrow{K}_H = \sum_{i=0}^{\infty}\left(\overleftrightarrow{K}_H\overleftrightarrow{\chi}^b\right)^i\overleftrightarrow{K}_H$$



DENSITY-DENSITY IN RECIPROCAL SPACE

$$\tilde{V}^{(1)}_{EXT}(\vec{q}) = \int_V d^3r \frac{e^{-i\vec{q}\vec{r}}}{\sqrt{V}} V^{(1)}_{EXT}(\vec{r})$$

$$\tilde{\rho}^{(1)}(\vec{q}) = \int_V d^3r \frac{e^{-i\vec{q}\cdot\vec{r}}}{\sqrt{V}} \rho^{(1)}_{EXT}(\vec{q})$$

$$\tilde{\rho}^{(1)}(\vec{q}) = \int_V d^3r d^3r' \frac{e^{-i\vec{q}\cdot\vec{r}}}{\sqrt{V}} \chi(\vec{r},\vec{r}') \sum_{q'} \frac{e^{i\vec{q}'\vec{r}'}}{\sqrt{V}} \tilde{V}^{(1)}_{EXT}(q')$$

(1) $$\tilde{\rho}^{(1)}(\vec{q}) = \sum_{q'} \tilde{\chi}(\vec{q},\vec{q}') \tilde{V}^{(1)}_{EXT}(\vec{q}')$$

$$\tilde{\chi}(\vec{q},\vec{q}') = \int_V d^3r d^3r' \frac{e^{-i\vec{q}\cdot\vec{r}}}{\sqrt{V}} \chi(\vec{r},\vec{r}') \frac{e^{i\vec{q}'\cdot\vec{r}'}}{\sqrt{V}}$$

$$G(\vec{r},\vec{r}') = \int_V d^3r'' K(\vec{r},\vec{r}'') \chi(\vec{r}'',\vec{r}')$$

$$\tilde{G}(\vec{q},\vec{q}') = \int_V d^3r\, d^3r'\, d^3r''\, d^3r''' \frac{e^{-i\vec{q}(\vec{r})}}{\sqrt{V}} \sum_{q''} K(\vec{r},\vec{r}'') \frac{e^{i\vec{q}''\cdot\vec{r}''}}{\sqrt{V}} \frac{e^{-i\vec{q}''\cdot\vec{r}'''}}{\sqrt{V}} \chi(\vec{r}''',\vec{r}') e^{+i\vec{q}'\vec{r}'}$$

(2) $$\tilde{G}(\vec{q},\vec{q}') = \sum_{q''} \tilde{K}(\vec{q},\vec{q}'') \tilde{\chi}(\vec{q}'',\vec{q}')$$

VECTOR NOTATION FOR RECIPROCAL SPACE

(1) → $\vec{\tilde{\rho}}^{(1)} = \vec{\tilde{\chi}}\, \vec{\tilde{V}}^{(1)}_{EXT}$

(2) → $\vec{\tilde{G}} = \vec{\tilde{K}}\, \vec{\tilde{\chi}}$

DENSITY-DENSITY RESPONSE

SAME EQUATIONS IN REAL AND RECIPROCAL SPACE WITH $(\rightsquigarrow, \rightsquigarrow)$ IN PLACE OF $(\rightarrow, \rightarrow)$

JELLIUM (SPATIALLY UNIFORM SYSTEMS)

$$\chi(\vec{r},\vec{r}') = f(\vec{r}-\vec{r}')$$

$$\tilde{\chi}(\vec{q},\vec{q}') = \int_V d^3r\, d^3r' \, \frac{e^{-i\vec{q}\vec{r}}}{\sqrt{V}} f(\vec{r}-\vec{r}') \frac{e^{i\vec{q}'\cdot\vec{r}'}}{\sqrt{V}}$$

$$= \int_V \frac{d^3r}{V} e^{-i(\vec{q}-\vec{q}')\cdot\vec{r}} \underbrace{\int d^3r'' \, e^{i\vec{q}\cdot\vec{r}''} f(\vec{r}'')}_{\equiv \text{def}}$$

$$= \delta_{\vec{q},\vec{q}'} \, \tilde{\chi}(\vec{q}) = \delta_{\vec{q},\vec{q}'} \, \tilde{\chi}(\vec{q},\vec{q})$$

$$\tilde{K}_H(\vec{q},\vec{q}') = \delta_{\vec{q},\vec{q}'} \frac{4\pi e^2}{q^2}$$

$$\tilde{K}_{xc}^{LDA}(\vec{q},\vec{q}') = f_{xc}(\rho)\, \delta_{\vec{q},\vec{q}'}$$

$$\chi^b(\vec{q},\vec{q}') = \delta_{\vec{q},\vec{q}'} \, \chi^b(\vec{q},\vec{q}) = \delta_{\vec{q},\vec{q}'} \, \chi^b(\vec{q})$$

$$\varepsilon^{-1}(\vec{q},\vec{q}') = \delta_{\vec{q},\vec{q}'} \, \varepsilon^{-1}(\vec{q},\vec{q}) = \delta_{\vec{q},\vec{q}'} \, \varepsilon^{-1}(\vec{q})$$

THE MATRIX EQUATION BECOMES A SCALAR EQUATION

$$\boxed{\varepsilon^{-1\,LDA}(\vec{q}) = \frac{1}{1 - \left[\frac{4\pi e^2}{q^2} + f_{xc}(\rho)\right] \chi^b(q)}}$$

$$\varepsilon^{-1\,RPA}(\vec{q}) = \frac{1}{1 - \frac{4\pi e^2}{q^2} \chi^b(q)}$$

COMPUTATION OF $\chi^b(\vec{q})$ IN JELLIUM (3D)

$$\chi^b(q) = \int_V d^3r\, d^3r' \frac{e^{-i\vec{q}\vec{r}}}{\sqrt{V}} \chi^b(\vec{r},\vec{r}') \frac{e^{i\vec{q}\vec{r}'}}{\sqrt{V}}$$

$$= \frac{4}{V} \sum_i \langle \psi_i^{(0)} | e^{-i\vec{q}\cdot\vec{r}}\, Q\, \frac{1}{\varepsilon_0^i - H^0}\, Q\, e^{i\vec{q}\cdot\vec{r}} | \psi_i^{(0)} \rangle$$

$$= \frac{4}{V} \sum_{\substack{\vec{k} \\ |\vec{k}|<k_F \\ |\vec{k}+\vec{q}|>k_F}} \frac{1}{\varepsilon_{\vec{k}} - \varepsilon_{\vec{k}+\vec{q}}} = 4 \int_{\substack{k<k_F \\ |\vec{k}+\vec{q}|>k_F}} \frac{d^3k}{(2\pi)^3} \frac{1}{\varepsilon_{\vec{k}} - \varepsilon_{\vec{k}+\vec{q}}}$$

$$= 4 \int_{\substack{\| \\ \|}}^{\;} \frac{d^3k}{(2\pi)^3} \frac{1}{\frac{\hbar^2k^2}{2m_e} - \frac{\hbar^2k^2}{2m_e} - \frac{\hbar^2q^2}{2m_e} - \frac{2\hbar^2\vec{q}\cdot\vec{k}}{2m_e}}$$

$$= -\frac{8m_e}{\hbar^2} k_F \int_{\substack{p<1 \\ |\vec{p}+\hat{x}x|}} \frac{d^3p}{(2\pi)^3} \frac{1}{x^2 + 2xp_x} \qquad x = \frac{q}{k_F}$$

$$DOS_{\text{AT } E_{FERMI}} = \frac{m_e k_F}{\pi^2 \hbar^2} \quad \text{(FOR THE 2 SPINS)}$$

LINDHARD FUNCTION

$$\chi^b(q) = -DOS \left[\frac{1}{2} + \frac{x^2-4}{8x} \ln \left| \frac{x-2}{x+2} \right| \right]$$

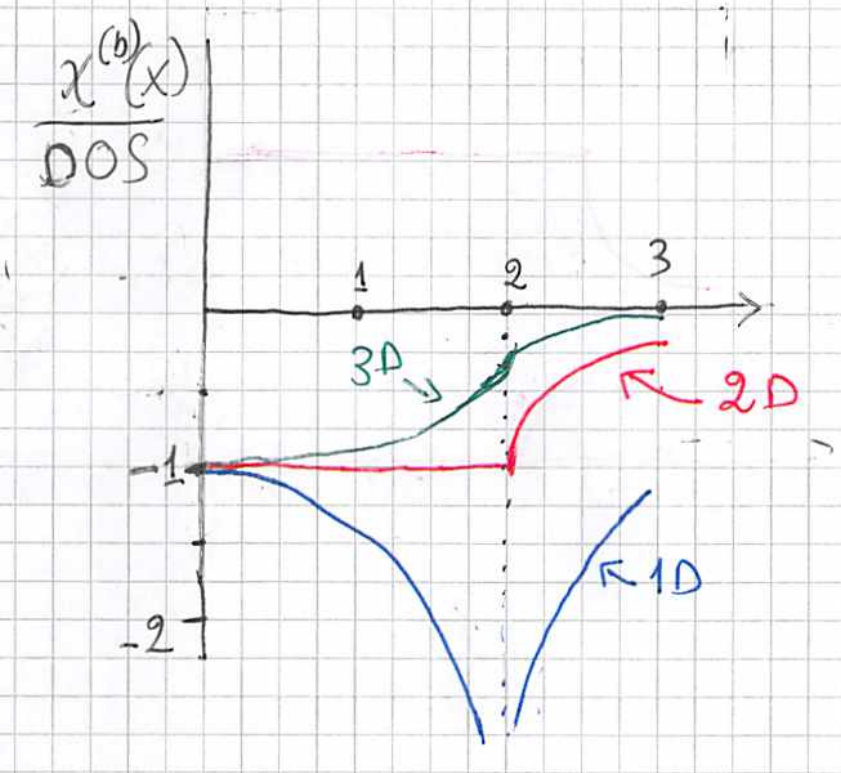
$\chi^b(q)$ IN 2D AND 1D

	2D	1D
$DOS_{E_{FERMI}}$	$\frac{m}{\pi\hbar^2}$	$\frac{2m}{\pi\hbar^2 k_F}$

$$x = \frac{q}{k_F}$$

$$\chi^b(q) = -DOS \times \begin{cases} \text{2D} \left[\frac{1}{x} - \theta(x-2)\frac{\sqrt{x^2-4}}{x} \right] \\ \text{1D} \left[\frac{1}{x} \ln\left| \frac{x+2}{x-2} \right| \right] \end{cases}$$

$$\theta(q) = \begin{cases} 1 & \text{se } x > 2 \\ 0 & \text{se } x < 2 \end{cases}$$



IN EACH DIMENSION THE FUNCTION OR ITS DERIVATIVE HAS A DISTONTINUITY AT $x=2$ $(q=2k_F)$!

LOWER IS THE DIMENTION THE STRONGER IS THE DISCONTINUITY

PHONON PERTURBATION IN RECIPROCAL SPACE

$\vec{q}$ = PHONON WAVE VECTOR

$\vec{R} + \vec{\tau}_\alpha$ = COORDINATE OF ATOM α IN THE UNIT CELL CENTERED IN $\vec{R}$

ATOM AT SITE $\vec{R}\alpha$ DISPLACED BY PHONON BY

$$\vec{u}_{\vec{R}\alpha} = \vec{u}_{\vec{q}\alpha} e^{i\vec{q}(\vec{R}+\vec{\tau}_\alpha)} = \sum_{c=x,y,z} \hat{c}\, u_{\vec{q}\alpha c}\, e^{i\vec{q}(\vec{R}+\vec{\tau}_\alpha)}$$

DYNAMICAL MATRIX

$$D_{\alpha c, \alpha' c'}(\vec{q}) = \frac{d^2 E}{du_{\alpha' c'}(-q)\, du_{\alpha c}(\vec{q})}$$

E = TOTAL ENERGY PER UNIT CELL

PHONONS AT $\vec{q}$

$\omega_\nu^2(\vec{q})$ = EIGENVALUES OF $\frac{1}{\sqrt{M_\alpha}} D^{(\vec{q})}_{\alpha c, \alpha' c'} \frac{1}{\sqrt{M_{\alpha'}}}$

M_α = MASS OF ATOM α

$\nu = 1, \ldots, 3N_{at}$ $\quad N_{at}$ = NUMBER OF ATOMS IN THE UNIT CELL

PHONON AS PERTURBATION IN DFT

UNPERTURBED POTENTIAL

$$V^{(0)}_{EXT}(\vec{r}) = \sum_{\vec{R}}^{\text{DIRECT LATTICE}} \sum_{\alpha} V_\alpha(\vec{r} - (\vec{R} + \vec{\tau}_\alpha)) \qquad V_\alpha(\vec{r}) = -\frac{e^2 Z_\alpha}{r}$$

(α: ATOM IN THE UNIT CELL)

[PHONON PERTURBATION OF WAVEVECTOR $\vec{q}$

ATOM AT SITE $\vec{R}\alpha$ DISPLACED BY

$$\vec{u}_{\vec{R}\alpha} = \vec{u}_{\vec{q}\alpha} e^{i\vec{q}(\vec{R}+\vec{\tau}_\alpha)} = \sum_{c=xyz} \hat{c}\, u_{\vec{q}\alpha c}\, e^{i\vec{q}(\vec{r}+\vec{\tau}_\alpha)}$$

FIRST DERIVATIVE OF THE EXTERNAL POTENTIAL

$$V^{(1)\,EXT}_{\vec{q}\alpha c}(\vec{r}) = \frac{dV_{EXT}(\vec{r})}{du_{\vec{q}\alpha c}} = \sum_{\vec{R}} e^{i\vec{q}(\vec{R}+\vec{\tau}_\alpha)} V^{(1)}_{\alpha c}(\vec{r} - (\vec{R}+\vec{\tau}_\alpha))$$

$$V^{(1)}_{\alpha c} = \frac{dV_\alpha(\vec{r} - \vec{u})}{du_c}$$

$$V^{(1)\,EXT}_{\vec{q}\alpha c}(\vec{r}) = e^{i\vec{q}\vec{r}}\, U^{EXT}_{q\alpha c}(\vec{r})$$

$$U^{EXT}_{\vec{q}\alpha c}(\vec{r}) = \sum_{\vec{R}} e^{-i\vec{q}(\vec{r} - (\vec{R}+\vec{\tau}_\alpha))} V^{(1)}_{\alpha c}(\vec{r} - (\vec{R}+\vec{\tau}_\alpha))$$

$U(\vec{r})$ IS CRYSTAL PERIODIC NAMELY

$$\forall \vec{R}' \in \text{DIRECT LATTICE} \quad U^{EXT}_{q\alpha c}(\vec{r}+\vec{R}') = U^{EXT}_{q\alpha c}(\vec{r})$$

WE SUPPOSE THAT THE SAME FACTORISATION HOLDS FOR $V^{KS}_{\vec{q}\alpha c}(\vec{r})$

LINEARLY PERTURBED WAVE FUNCTION

→ PERTURBATION IS NOT HERMITIAN

$$\left[V^{(1)\,EXT}_{\vec{q}}(\vec{r})\right]^* = V^{(1)\,EXT}_{-\vec{q}}(\vec{r})$$

→ IT CAN BE SEEN AS A LINEAR SUPERPOSITION OF HERMITIAN PERTURBATION ON EACH $\vec{R}_\alpha$ ATOM WITH PHASE $e^{i\vec{q}(\vec{R}+\vec{\tau}_\alpha)}$

$$|\Psi^{(e)}_{\vec{k}i}\rangle = \text{BLOCH WAVEFUNCTION} = \frac{e^{i\vec{k}\cdot\vec{r}}}{\sqrt{N}}\,|u^{(e)}_{\vec{k}i}\rangle$$

PERIODIC PART OF BLOCH WAVE FUNCTION NORMALIZED IN THE UNIT CELL

$\sqrt{N}$ ↑ NUMBER OF UNIT CELLS

$$H^{(0)}_{\vec{k}}|u_{\vec{k}i}\rangle = \varepsilon^{(0)}_{\vec{k}i}|u^{(0)}_{\vec{k}i}\rangle$$

$$H^{(e)}_{\vec{k}} = \frac{1}{2m}(p+\hbar\vec{k})^2 + V^{(0)}(\vec{r})$$

$$|\Psi^{(\vec{q}ac)}_{\vec{k}i}\rangle = \sum_{\vec{k}'}\sum_{j}^{\text{EMPTY STATES}} |\Psi^{(0)}_{\vec{k}'j}\rangle \frac{\langle\Psi^{(0)}_{\vec{k}'j}|e^{i\vec{q}\vec{r}}U^{KS}_{\vec{q}ac}(\vec{r})|\Psi^{(e)}_{\vec{k}i}\rangle}{\varepsilon^{(0)}_{\vec{k}i} - \varepsilon^{(0)}_{\vec{k}'j}}$$

UNIT CELL PERIODIC

INTEGRATION OVER UNIT CELL

$$\langle\Psi^{(0)}_{\vec{k}'j}|e^{i\vec{q}\vec{r}}U(\vec{r})|\Psi^{(e)}_{\vec{k}i}\rangle = \langle u^{(0)}_{\vec{k}'j}|e^{i(\vec{k}+\vec{q}-\vec{k}')\vec{r}}U(\vec{r})|u^{(0)}_{\vec{k}i}\rangle \times \sum_{\vec{R}}^{N\text{-CELLS}} \frac{e^{i(\vec{k}+\vec{q}-\vec{k})\vec{R}}}{N}$$

↑ INTEGRATION OVER THE N-UNIT CELL HILBERT SPACE

RECIPROCAL VECTORS

INTEGRATION OVER UNIT CELL

$$= \sum_G \delta_{\vec{k}+\vec{q}-\vec{k}',\vec{G}} \underbrace{\langle u^{(0)}_{\vec{k}'j} | e^{i\vec{G}\cdot\vec{r}} U(\vec{r}) | u^{(0)}_{\vec{k}i} \rangle}$$

$$\Downarrow$$

$$|\psi^{(\vec{q}\alpha c)}_{\vec{k}i}\rangle = \frac{1}{\sqrt{N}} e^{i(\vec{k}+\vec{q})\vec{r}} \underbrace{|v^{(\vec{q}\alpha c)}_{\vec{k}i}\rangle}$$

CELL PERIODIC FUNCTION

$$|v^{(\vec{q}\alpha c)}_{\vec{k}i}\rangle = \sum_j^{\text{EMPTY}} |u^{(0)}_{\vec{k}+\vec{q}j}\rangle \frac{\langle u^{(0)}_{\vec{k}+\vec{q}j} | U^{KS}_{\vec{q}\alpha c}(\vec{r}) | u^{(0)}_{\vec{k}i}\rangle}{\varepsilon^{(0)}_{\vec{k}i} - \varepsilon^{(0)}_{\vec{k}+\vec{q}j}}$$

$$= \frac{1}{\varepsilon^{(0)}_{\vec{k}i} - H^{KS}_{\vec{k}+\vec{q}}} Q_{\vec{k}+\vec{q}} U^{KS}_{\vec{q}\alpha c}(\vec{r}) | u^{(0)}_{ke}\rangle$$

$$Q_{\vec{k}+\vec{q}} = \mathbb{1} - P_{\vec{k}+\vec{q}}$$

$$P_{\vec{k}+\vec{q}} = \sum_i^{occ} |u^{(0)}_{\vec{k}+\vec{q}i}\rangle \langle u^{(0)}_{\vec{k}+\vec{q}i}|$$

$$d^{\alpha c\,(KS)}_{\vec{k}+\vec{q}j\,\vec{k}i} = \langle u^{(0)}_{k+qj} | U^{(KS)}_{\vec{q}\alpha c} | u^{(0)}_{\vec{k}i}\rangle =$$

ELECTRON PHONON MATRIX ELEMENT

INDUCED CHARGE DENSITY

$$\rho^{(1)}_{\vec{q}\alpha c}(\vec{r}) = e^{i\vec{q}\vec{r}}\, n^{(1)}_{\vec{q}\alpha c}(\vec{r})$$

$n^{(1)}_{\vec{q}\alpha c}$: PERIODIC IN THE UNIT CELL

$$n^{(1)}_{\vec{q}\alpha c} = \frac{1}{N} 2 \sum_{i\vec{k}} \left[\langle u^{(0)}_{\vec{k}i} | \vec{r} \rangle \langle \vec{r} | V^{(\vec{q}\alpha c)}_{\vec{k}i} \rangle + \langle V^{(-\vec{q}\alpha c)}_{\vec{k}i} | \vec{r} \rangle \langle \vec{r} | u^{(0)}_{\vec{k}i} \rangle \right]$$

(2: SPIN)

$$V^{(1)}_{H\&C}(\vec{r}) = \int d^3r'\, K_{Hxc}(\vec{r},\vec{r}')\, e^{i\vec{q}\vec{r}}\, n^{(1)}_{\vec{q}\alpha c}(\vec{r}')$$

$$\Downarrow\Downarrow$$

$$V^{(1)}_{Hxc}(\vec{r}) = e^{i\vec{q}\vec{r}}\, U^{(1)}_{Hxc}(\vec{r})$$

$U^{(1)}_{Hxc}$: PERIODIC FUNCTION IN THE UNIT CELL

SECOND DERIVATIVE OF THE EXTERNAL POTENTIAL

$$V^{(1,1)\,EXT}_{\vec{q}\alpha c\,-\vec{q}\alpha' c'}(\vec{r}) = \sum_{\vec{R}} e^{i\vec{q}(\vec{R}+\vec{\tau}_\alpha)}\, e^{-\vec{q}(\vec{R}+\vec{\tau}_{\alpha'})}\, \delta_{\alpha\alpha'}\, V^{(1,1)}_{\alpha cc'}(\vec{r}-(\vec{R}+\vec{\tau}_\alpha))$$

$$= \delta_{\alpha\alpha'} \sum_{\vec{R}} V^{(1,1)}_{\alpha cc'}(\vec{r}-(\vec{R}+\vec{\tau}_\alpha)) = \text{CELL PERIODIC INDEP OF } \vec{q}$$

$$V^{(1,1)}_{\alpha cc'}(\vec{r}) = \frac{\partial^2 V_\alpha(\vec{r}-\vec{u})}{\partial u_c \partial u_{c'}}$$

DYNAMICAL MATRIX

STRONG DEPENDENCE ON $\vec{q}$ IN A METAL

$$D_{c\alpha,\alpha' c'}(q) = \overset{\text{SPIN}}{2} \sum_{\vec{R}} \sum_{i}^{occ} \Big[\langle \psi^{(-q\alpha' c')}_{\vec{k}i} | V^{(1)\,EXT}_{\vec{q}\alpha c} | \psi^{(0)}_{\vec{k}i} \rangle + \langle \psi^{(0)}_{\vec{k}i} | V^{(1)\,EXT}_{-\vec{q}\alpha c} | \psi^{(q\alpha' c')}_{\vec{k}i} \rangle \Big]$$

$$+ \int d^3r\, \rho^{(0)}(\vec{r})\, V^{(1,1)\,EXT}_{\vec{q}\alpha c,\,-\vec{q}\alpha' c'}(\vec{r}) + \frac{\partial^2 E_{II}}{\partial u_{\alpha' c'}(-\vec{q})\, \partial u_{\alpha c}(\vec{q})}$$

WEAK DEPENDENCE ON $\vec{q}$

FIRST TERM $= \Pi_{c\alpha,\alpha' c'}(\vec{q})$

$$\Pi_{c\alpha,\alpha' c'}(\vec{q}) = 2\,\frac{1}{N} \sum_{\vec{k}} \sum_{i}^{occ} \sum_{j}^{EMPTY} \frac{\Big[d^{\alpha' c'\,KS}_{\vec{k}i,\vec{k}+\vec{q}j}\, d^{\alpha c\,EXT}_{\vec{k}+\vec{q}j,\,\vec{k}i} + d^{\alpha c\,EXT}_{\vec{k}i,\vec{k}+\vec{q}j}\, d^{\alpha' c'\,KS}_{\vec{k}+\vec{q}j,\,\vec{k}i} \Big]}{\varepsilon^{(0)}_{\vec{k}i} - \varepsilon^{(0)}_{\vec{k}+\vec{q}j}}$$

NUMERATOR SMOTH FUNCTION OF $\vec{q}$

APPROXIMATION → REPLACE IT BY A CONSTANT

$$\Pi_{\alpha,\alpha'}(\vec{q}) = 2C \int \frac{dk}{(2\pi)^D} \sum_i^{occ} \sum_j^{EMPTY} \frac{1}{\varepsilon^{(0)}_{\vec{k}i} - \varepsilon^{(0)}_{\vec{k}+\vec{q}j}}$$

(D = DIMENSION OF THE SPACE)

$\Pi(\vec{q})$ → DISCONTINUITIES WHEN DENOMINATOR GOES TO ZERO

IN THE CASE OF A SINGLE PARABOLIC BAND

$$\Pi_{\alpha,\alpha'}(\vec{q}) \propto 2C \int_{\substack{|\vec{k}|<k_F \\ |\vec{k}+\vec{q}|>k_F}} \frac{d^D k}{(2\pi)^D} \frac{1}{\varepsilon^{(0)}_{\vec{k}} - \varepsilon^{(0)}_{\vec{k}+\vec{q}}} \propto \text{LINDHAD FUNCTION IN D DIMENSIONS}$$

$\Downarrow$

$\hbar\omega(\vec{q})$ DISCONTINUITIES AT $|\vec{q}| = 2k_F$

$\Downarrow$

KOHN ANOMALIES

RESPONSE TO A UNIFORM ELECTRIC FIELD: SUSCEPTIBILITY

3x3 MATRIX

$$\Delta \vec{P} = \overleftrightarrow{\chi}\, \vec{E}$$

$\Delta \vec{P}$: POLARISATION PER UNIT VOLUME

$\vec{E}$: UNIFORM ELECTRIC FIELD

$$\overleftrightarrow{\varepsilon}_r = \begin{matrix}\text{CLASSICAL}\\ \text{ELECTROSTATIC}\\ \text{DIELECTRIC}\\ \text{CONSTANT}\end{matrix} = \overleftrightarrow{1} + (4\pi)\,\overleftrightarrow{\chi}$$

(4π) IN G.G.S GAUSS UNITS

NOTICE THAT $\vec{E}$ IS THE AVERAGE ELECTRIC FIELD AND NOT THE EXTERNAL ONE (THAT CORRESPOND TO THE $\vec{D}$ FIELD OF ELECTROSTATIC)

IF $\mathcal{E}(\vec{E})$ ELECTRONIC ENERGY PER UNIT VOLUME

$$\overleftrightarrow{\chi} = -\frac{d^2\mathcal{E}(\vec{E})}{d\vec{E}\,d\vec{E}}$$

BARE POT.

$$V_\alpha^{(1)B}(\vec{r}) = e\, r_\alpha \qquad \alpha = x,y,z \nearrow \text{FIELD DIRECTION}$$

$$|e| = e$$

$$V_\alpha^{(1)SC}(\vec{r}) = V_\alpha^{(1)B}(\vec{r}) + \int d^3r'\, K_{HxC}(\vec{r},\vec{r}')\, \rho_\alpha^{(1)}(\vec{r}') \qquad \left(V_\alpha^{(1)HxC}(\vec{r})\right)$$

[NOTICE THAT SINCE $\vec{E} \neq$ EXTERNAL $V_H^{(1)}(\vec{r})$ DOES NOT CONTAIN THE TERMS ASSOCIATED TO THE MACROSCOPIC (UNIFORM ON THE UNIT CELL SCALE) ELECTRIC FIELD DUE, E.G., TO CRYSTAL SURFACE]

PERTURBATION THEORY REQUIRES THE CALCULATION OF

$$\langle \psi_{\vec{k}_j} | r_\alpha | \psi_{\vec{k}_i} \rangle \stackrel{?}{=}$$

WHERE $H|\psi_{\vec{k}_i}\rangle = \varepsilon_{\vec{k}_i}|\psi_{\vec{k}_i}\rangle$

AND $\varepsilon_{\vec{k}_i} \neq \varepsilon_{\vec{k}_j}$

$$= \int_{\substack{N \\ \text{CELLS}}} d^3r \frac{e^{i(\vec{k}_i - \vec{k}_j)\vec{r}}}{N} u^*_{\vec{k}_j}(\vec{r})\, u_{\vec{k}_i}(\vec{r})\, r_\alpha$$

= ILL DEFINED INTEGRAL SINCE IT DEPENS ON THE CHOICE OF THE CELL (ON ITS BORDERS)

THE EXPECTATION VALUE OF r_α IS WELL DEFINED IN A FINITE SYSTEM AND

$$[r_\alpha, H] = i\frac{\hbar}{m_e} p_\alpha \qquad \text{IF} \quad H|\psi_i\rangle = \varepsilon_i|\psi_i\rangle$$

$$\langle \psi_j | (r_\alpha H - H r_\alpha) | \psi_i \rangle = \frac{i\hbar}{m_e} \langle \psi_j | p_\alpha | \psi_i \rangle$$

$$\langle \psi_j | r_\alpha | \psi_i \rangle = \frac{i\hbar}{m_e} \frac{\langle \psi_j | p_\alpha | \psi_i \rangle}{\varepsilon_i - \varepsilon_j}$$

WE SUPPOSE THAT THIS EQUALITY IS VALID ALSO IN SOLID (VERIFIED IN ESERCITAZIONE 4)

$$\langle \psi_{\vec{k}'_j} | r_\alpha | \psi_{\vec{k}_i} \rangle = \delta_{\vec{k}',\vec{k}} \frac{i\hbar}{m_e} \frac{\langle u_{\vec{k}_j} | p_\alpha | u_{\vec{k}_i} \rangle}{\varepsilon_{\vec{k}_i} - \varepsilon_{\vec{k}_j}}$$

$$\chi_{\alpha\beta} = -2 \int \frac{d^3k}{(2\pi)^3} \sum_i^{\text{OCC}} \sum_j^{\text{EMPTY}} \frac{1}{\varepsilon_{\vec{k}i} - \varepsilon_{\vec{k}j}} \times$$

(SPIN)

$$\Big[\langle u_{\vec{k}i} | \frac{i\frac{\hbar e}{m_e} P_\alpha}{\varepsilon_{\vec{k}j} - \varepsilon_{\vec{k}i}} + V_\alpha^{(1)Hxc}(\vec{r}) | u_{\vec{k}j} \rangle \langle u_{\vec{k}j} | \frac{i\frac{\hbar e}{m_e} P_\beta}{\varepsilon_{\vec{k}i} - \varepsilon_{\vec{k}j}} | u_{\vec{k}i} \rangle$$

$$+ \langle u_{\vec{k}i} | \frac{i\frac{\hbar e}{m_e} P_\beta}{\varepsilon_{\vec{k}j} - \varepsilon_{\vec{k}i}} | u_{\vec{k}j} \rangle \langle u_{\vec{k}j} | \frac{i\frac{\hbar e}{m_e} P_\alpha}{\varepsilon_{ki} - \varepsilon_{\vec{k}j}} + V_\alpha^{(1)Hxc} | u_{\vec{k}i} \rangle \Big]$$

IF WE NEGLEGT $V_\alpha^{(1)Hxc}$ ERROR $\sim 10-20\%$ IN SEMICONDUCTOR, LARGER ERROR WHEN THE DENSITY IS MODULATED (MOLECULAR CRYSTALS)

NEGLECTING $V_\alpha^{(1)Hxc}$:

$$\chi_{\alpha\alpha} \simeq 4\left(\frac{\hbar e}{m_e}\right)^2 \int \frac{d^3k}{(2\pi)^3} \sum_i^{\text{OCC}} \sum_j^{\text{EMP}} \frac{|\langle u_{\vec{k}j} | P_\alpha | u_{ki} \rangle|^2}{(\varepsilon_{\vec{k}j} - \varepsilon_{\vec{k}i})^3}$$

OTHER DERIVATIVES OF THE POLARISATION

λ = HAMILTONIAN PARAMETER (E.G. ATOMIC POSITION)

H^{λ}

$$\frac{d\vec{P}(\lambda)}{d\lambda} = -\frac{d\mathcal{E}}{d\lambda d\vec{E}} = 2\int \frac{d^3k}{(2\pi)^3} \sum_i^{occ} -|e| \Big[$$

PROJECTOR IN THE EMPTY SUBSPACE

$$\frac{d\langle u_{\vec{k}i}|}{d\lambda} Q_{\vec{k}} \vec{r} |u_{\vec{k}i}\rangle + \langle u_{\vec{k}i}| \vec{r} Q_{\vec{k}} \frac{d|u_{\vec{k}i}\rangle}{d\lambda} \Big] =$$

OR EMPTY

$$= -|e| 2 \int \frac{d^3k}{(2\pi)^3} \sum_i^{occ} \sum_{j\neq i}^{(ALL)} \Big[\frac{d\langle u_{\vec{k}i}|}{d\lambda} |u_{\vec{k}j}\rangle \frac{\langle u_{\vec{k}j}| \frac{i\hbar}{m_e} (\vec{P} + \hbar\vec{k}) |u_{\vec{k}i}\rangle}{\mathcal{E}_{\vec{k}i} - \mathcal{E}_{\vec{k}j}}$$

($\frac{dH_{\vec{k}}}{d\vec{k}}$)

$$- \langle u_{\vec{k}i}| \frac{i\hbar}{m_e} (\vec{P} + \hbar\vec{k}) |u_{\vec{k}j}\rangle \frac{\langle u_{\vec{k}j}| \frac{d|u_{\vec{k}i}\rangle}{d\lambda}}{\mathcal{E}_{\vec{k}i} - \mathcal{E}_{\vec{k}j}} \Big]$$

($\frac{dH_{\vec{k}}}{d\vec{k}}$)

$$= -2|e| i \int \frac{d^3k}{(2\pi)^3} \sum_i^{occ} \Big[\frac{d\langle u_{\vec{k}i}|}{d\lambda} \frac{d|u_{\vec{k}i}\rangle}{d\vec{k}} - \frac{d\langle u_{\vec{k}i}|}{d\vec{k}} \frac{d|u_{\vec{k}i}\rangle}{d\lambda} \Big]$$

IF λ = DISPLACEMENT OF ATOMS

WITH $\vec{q} = 0$

$\Downarrow$

$\frac{d\vec{P}(\lambda)}{d\lambda}$ EFFECTIVE CHARGES FOR THE IR ACTIVITY